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RING-OPENING POLYMERIZATION OF STRAINED CYCLOTETRASILANES AS A NEW ROUTE TOWARDS WELL DEFINED POLYSILYLENES

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Abstract: Ring-opening polymerization of cyclic silanes is described as a new synthetic route to well defined high molecular weight polysilylenes. Strained cyclotetrasilanes with phenyl and methyl substituents at each Si atom in the four-membered ring are prepared by partial dephenylation of octaphenylcyclotetrasilane with triflic acid and subsequent treatment with methylmagnesium bromide. Chemoselectivity, regioselectivity and stereoselectivity of monomer synthesis is discussed in detail. In addition to classic anionic initiators for the ring-opening process, new catalysts and initiators based on transition metals (Cu, Pd, Pt) are described. They provide much better control of the microstructure than systems with Li⁺ counterion.

INTRODUCTION

Recent interest in polysilylenes (polysilanes) originates in the unusual and attractive properties of these polymers^{1,2,3}. There are a few current and potential applications for these polymers. Polysilylenes are used as precursors to silicon carbide fibers, as photoconductors, photoresists, nonlinear optical materials, as well as initiators for radical polymerization. These polymers with a linear Si-Si catenation reaching more than 1,000 Si atoms in the main chain only recently have been prepared as soluble and tractable materials. Polysilylenes behave differently than most organic polymers. They strongly absorb in the range of 300 to 400 nm with the extinction coefficient and absorption maximum depending on the chain conformation and nature of substituents. They form easily radical anions and radical cations, in a way similar to polyenes. Symmetrically substituted polymers do not transform to the isotropic melt but rather form columnar mesophases. These polymers are thermodynamically unstable and can be easily degraded to cyclooligosilanes. The degradation can be accomplished by light but also thermally as well as in the presence of anionic intermediates.

Most properties of polysilylenes depend strongly on substituents at silicon atom as well as on the chain conformation. Some applications, especially in the optoelectronics, as well as correct structure-property studies require preparation of well defined polymers. They should have controlled molecular weight, narrow molecular weight distribution, desired functional groups along the chain and at the chain end, as well as controlled microstructure. It is also interesting to compare properties of various copolymers with a random and a regular (blocky and periodic) structures and to establish influence of the tacticity on chain conformation and on spectroscopic and electronic properties.

Polysilylenes are typically prepared by the reductive coupling of disubstituted dichlorosilanes with alkali metals⁴ and by dehydrogenative coupling of primary silanes⁵. In both cases polymers with a broad molecular weight distribution and uncontrolled molecular weights are formed. We improved a control of some parameters of the reductive coupling process by using low temperature sonochemical technique⁶. Some side reactions were suppressed and also polymers with very high molecular weight ($M > 100,000$) were selectively degraded by friction forces operating during the cavitation process. Nevertheless, no control of the end groups and no control of tacticities was possible in this system. Polysilylenes can be also prepared by the anionic polymerization of so called masked disilenes, i.e. adducts of disilenes to aromatic compounds such as biphenyl or naphthalene⁷. This technique provides very good control of various structural features of polysilylenes and enables preparation of block copolymers. It can not be, however used to prepare polymers with aryl groups.

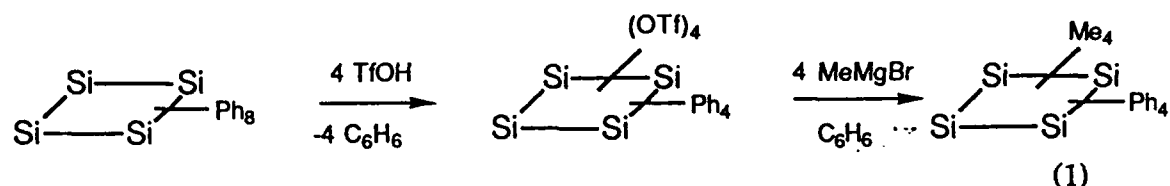
We have previously reported on the synthesis of strained cyclotetrasilanes which can be anionically polymerized to high molecular weight polysilylenes^{8,9}. This method allows preparation of polymers with aryl groups, too. In this paper we will discuss in more details the synthesis and characterization of some of cyclosilanes and use of some new catalytic systems for ring-opening polymerization.

RESULTS AND DISCUSSION

Monomer Synthesis/Triflation

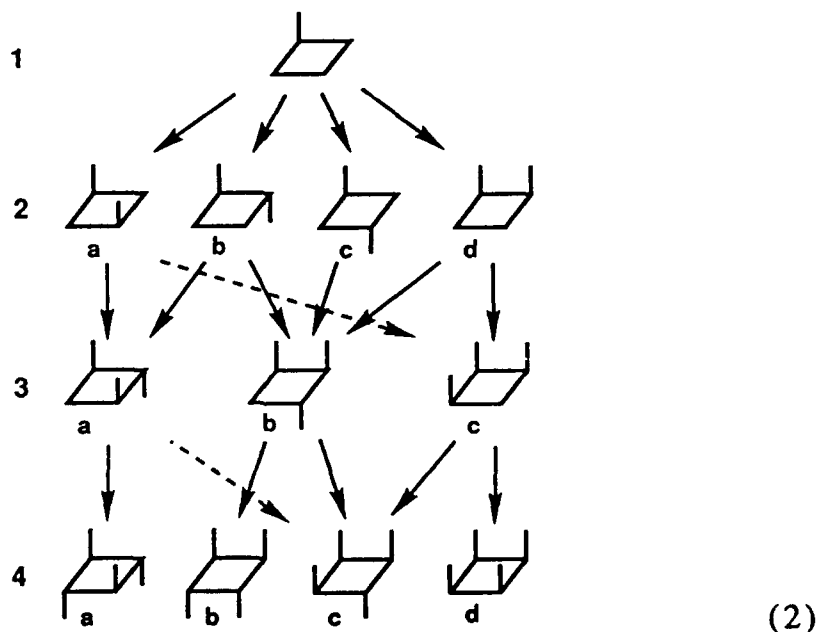
Most cyclopolysilanes described in literature are strainless and can not be used for polymerization. Reductive coupling usually produces rings which can not be polymerized by ring opening process. Generally the preferred ring size decreases with bulkiness of substituents and for dimethyl system the six-membered ring is preferred, for methylphenyl system the cyclopentasilane dominates, for diphenyl system the cyclotetrasilane is formed in large amount,

and a mixture of cyclotrisilane and disilene is formed with even more bulky dimesityl system. We have previously described the rapid and efficient dearylation of phenyl groups from different silanes using triflic acid. This reaction can also be applied to octaphenylcyclotetrasilane. Up to four phenyl groups can be removed from this ring before any ring cleavage is noticed. The resulting 1,2,3,4-tetraphenyl-1,2,3,4-tetrakis(trifluoromethane-sulfonate)cyclo-tetrasilane can be then converted by the action of methyl magnesium bromide to polymerizable 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclo-tetrasilane:



It was interesting to follow the chemoselectivity and stereoselectivity of the dearylation and methylation process in order to better control structure of possible isomers of the polymerizable rings and also to optimize conditions of the synthesis.

The structures of possible isomers are shown in the Scheme 2 below. The substituents in the ring may symbolize triflate or methyl groups, whereas phenyl groups are not shown:



The reaction was performed in CH_2Cl_2 increasing the $[\text{TfOH}]/[(\text{Ph}_2\text{Si})_4]$ ratios: from 0.5 to 5 mol/mol (H_2O and O_2 concentrations were below 1 ppm). The ^{19}F NMR spectra show several signals of various intensities (Fig. 1). A compilation of spectra enabled the tentative assignment of the signals. The positions of these signals shift downfield with increasing order of substitution.

After addition of 0.5 equivalent of TfOH a singlet corresponding to $(\text{TfO})\text{Ph}_7\text{Si}_4$ and 4 signals corresponding to the 4 isomers of $(\text{TfO})_2\text{Ph}_6\text{Si}_4$ were observed (rel. intensity 7:4:3:2). There are four isomers of $(\text{TfO})_2\text{Ph}_6\text{Si}_4$ (Scheme 2, 2a,b,c,d). With further addition of TfOH, the signal ascribed to $(\text{TfO})\text{Ph}_7\text{Si}_4$ disappeared, and 2 signals corresponding to $(\text{TfO})_3\text{Ph}_5\text{Si}_4$ increase in intensity. At $[\text{TfOH}]/[(\text{Ph}_2\text{Si})_4]=3$ there were two main signals with a ratio 2:1 ascribed to $(\text{TfO})_3\text{Ph}_5\text{Si}_4$ (3a). With continuous addition of the acid, the signals attributed to $(\text{TfO})_4\text{Ph}_4\text{Si}_4$ (approx. ratio 4:4:1) appeared. Addition of a 5th equivalent of triflic acid resulted in broadening of signals making spectra difficult to resolve.

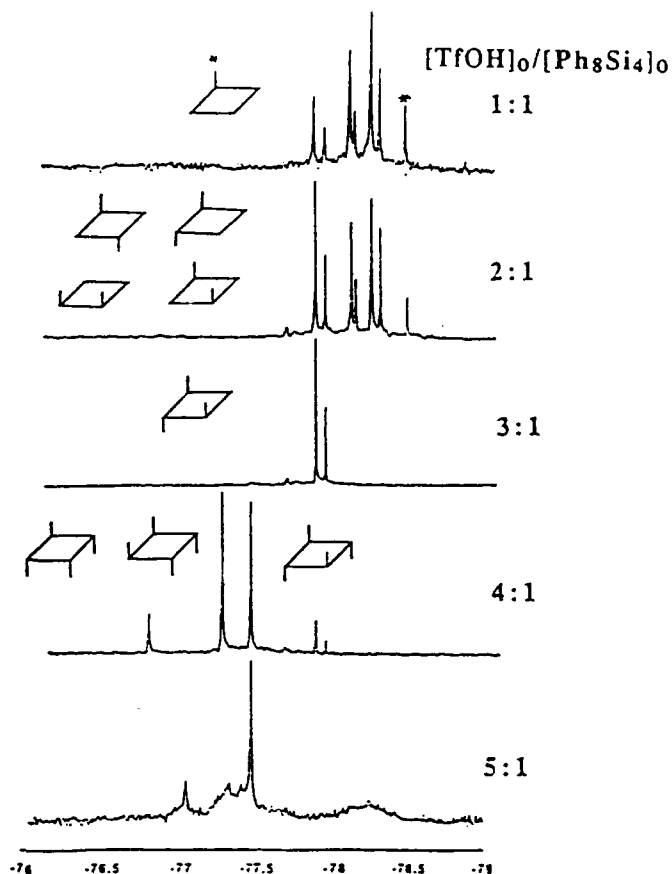


Fig. 1. ^{19}F NMR spectra recorded during triflation of octaphenylcyclotetrasilane

The triflation reaction is very fast up to 3 equivalents of the acid added (it had been completed before the first spectrum was taken). The reaction slows down considerably when the fourth equivalent of TfOH is added. The signal of the free acid is present in the solution for several hours and the progress of the substitution can be followed by NMR. Some broadening of the signal of triflic acid and of two signals of tetrakis(triflate) isomers was observed. The signals become sharp when the acid is consumed (ca. 6 hrs, 25°C , $[(\text{Ph}_2\text{Si})_4]_0=0.05$ mol/L). In the case of $[\text{TfOH}]/[(\text{Ph}_2\text{Si})_4]=5$, free acid is present in the mixture even after 24 hrs.

The triflated cyclotetrasilanes were characterized also by INEPT ^{29}Si NMR. All compounds show two groups of signals: one in the range 13 to 33 ppm corresponding to SiOTf moiety, the other in the range -20 to -30 ppm, typical for $>\text{SiPh}_2$ group. The chemical shifts of triflated silicon nuclei change upfield with the number of triflic groups in the ring. Monotriflate as well as all four isomers of bis(triflate) have been identified in the spectra. Four signals corresponding to tris(triflate) isomers were observed in the SiOTf range. Two main peaks (20.5, 19.4 ppm, approx. ratio 2:1) have been ascribed to the isomer predominant in the mixture. Only two signals were observed for

tetrakis(triflate) cyclotetrasilane Previous studies of the reactivity of phenyl silanes towards triflic acid revealed that the presence of a triflate moiety inhibits displacement at the same silicon atom and reduces the rate of dearylation at neighboring silicon atoms¹⁰. The NMR data are in agreement with these results showing that the rate of the dearylation reaction drops with the number of triflate groups introduced to the silane molecule. The selectivity of the reaction increases with the degree of substitution. Thus, bis(triflate) may be obtained with ca. 70% yield, while tris- and tetrakis(triflates) are formed in over 90% yield. The selectivity of triflation is relatively low at the stage of monotriflate, because the reaction is heterogeneous (the solubility of octaphenylcyclotetrasilane in CH_2Cl_2 is below 1%). Monotriflate is more soluble and undergoes further triflation in solution. Cyclotetrasilane containing five triflate groups in the molecule cannot be obtained selectively since the substitution reaction of the second phenyl for a triflate group at silicon atom is very slow and is accompanied by electrophilic ring cleavage by the acid.

Monomer Synthesis/Substitution

The samples containing 3, 4 and 5 equivalents of TfOH were methylated using MeMgBr and the ^1H NMR spectra of the methylated cyclotetrasilanes were correlated with the ^{19}F NMR spectra of triflate derivatives. This helped to assign signals to particular cyclic silanes and their isomers. The relative intensities of the isomers of disubstituted cyclics are similar in the corresponding ^{19}F and ^1H NMR spectra. This may indicate high stereoselectivity in the reaction of silyl triflates with Grignard reagent.

The ^1H NMR spectrum of the 3:1 mixture reveals, the main isomer of trimethylcyclotetrasilane, 3a. The ^1H NMR spectrum of the 4:1 reaction mixture shows 5 signals corresponding to tetramethylcyclotetrasilane isomers⁹. In the case of the 5:1 mixture, the ^1H NMR spectrum of the methyl region reveals 55% unreacted tetramethyl derivative, signals probably corresponding to pentamethyl cyclics (δ : 0.3-0.5 ppm) and to linear 1,1,2,3,4-pentamethyl-1,2,3,4-tetraphenyltetrasilane (δ : 0.0-0.06 ppm, 15%). The SiH multiplet at $\delta = 4.15$ ppm, confirmed the presence of the opened silane structure.

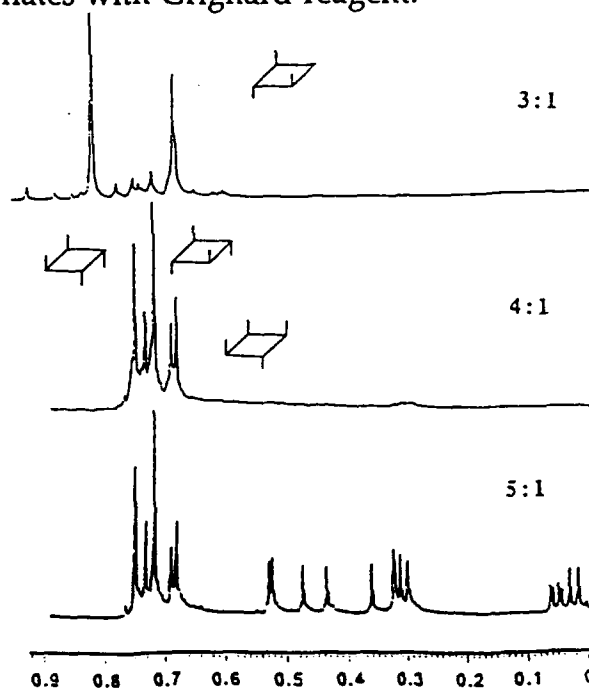


Fig. 2. ^1H NMR spectra of methylated cyclotetrasilanes at various content of Me groups per ring

Scheme 2 showed the formal transformation of isomers during the triflation/substitution process. A comparison of the ^1H and ^{19}F NMR spectra of the corresponding cyclotetrasilanes indicates highly stereoselective reaction of triflates with a Grignard reagent. The relative proportion of isomers is preserved during methylation. In other words, the proportion of isomers is established during the triflation process. The relative content of isomers does not correspond to a statistical distribution but rather to steric effects. Triflate group is the most bulky one, followed by phenyl and methyl. The content of a particular isomer of the triflated ring might be related to its steric constraints, especially for triflate groups which can exchange at the level of trisubstituted and tetrasubstituted isomers (and probably disubstituted ones, too). In the case of disubstituted rings, 2c isomer should be the most stable and should dominate the reaction products. Two others (presumably 2a, 2b) appear in similar amounts while the most hindered one (2d) should be formed in a minor quantity (Fig. 1).

The ^{19}F NMR spectrum of the $[\text{TfOH}]/[(\text{Ph}_2\text{Si})_4]=4$ mixture shows only three tetrakis(triflate) signals while there are five signals in the ^1H NMR spectrum. (There are four isomers of tetrasubstituted rings possible, which should give six signals total, but the most hindered one (4d) is probably not formed). Some fluorine signals for tetrakis(triflate) isomers can coincidentally overlap each other. In fact, the triflate groups in positions 1 and 3 in 4c are shielded similarly to the ones in 4b while the triflate group in position 4 would be shielded as in 4a. Only the triflate group in position 2 is different and it appears downfield from the others.

Exchange of triflate groups occurs very rapidly in less sterically hindered silyl triflates, e.g. Me_3SiOTf . In the case of phenyl(triflate)cyclotetrasilanes, fast exchange should lead to the thermodynamic mixture of stereoisomers at each stage of substitution. The dearylation reaction at $[\text{TfOH}]/[(\text{Ph}_2\text{Si})_4]<3$ is so fast that the exchange cannot be directly observed by NMR, since the acid is consumed very rapidly. However, the substitution of the fourth phenyl group is slow enough to make such observations possible.

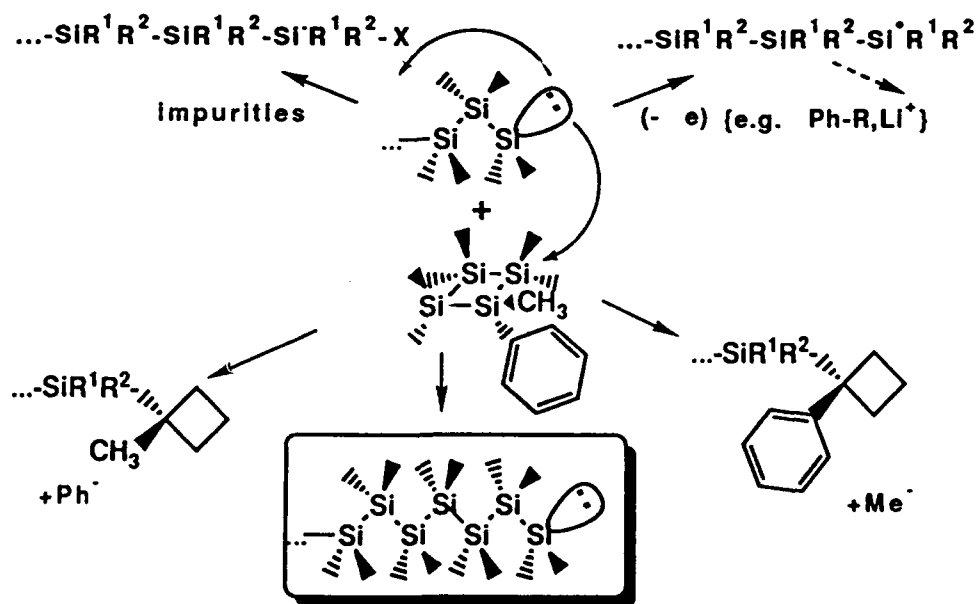
Both reactions, dearylation and ester group exchange, probably compete leading to a thermodynamically preferred mixture of isomers. The proportion of isomers (within accuracy of integration) is independent of the $[\text{TfOH}]/[(\text{Ph}_2\text{Si})_4]$ ratio (Fig. 1). Kinetic isomer distribution should be observed at a low acid/silane ratio. The distribution should change towards a thermodynamic proportion of isomers as the amount of TfOH and the lifetime of the acid in the reaction mixture increase. The exchange occurs at the stage of substitution of the third triflate group. Isomer 3a can be directly formed from isomers 2a and 2b, which both constitute approximately 50% of bis(triflate)cyclotetrasilane, while the concentration of isomer 3a among the

tris(triflate) cyclics exceeds 85%. This proves that at this stage, the exchange of ester groups must be faster than the dearylation. The substitution of the fourth phenyl group is even slower so the exchange must also take place, leading to the thermodynamically controlled mixture of isomers.

It is difficult to separate triflated and methylated derivatives since they are very sensitive to moisture and oxygen. However, repeated crystallization from hexane at low temperatures allows enhancement of 4a up to >90% purity.

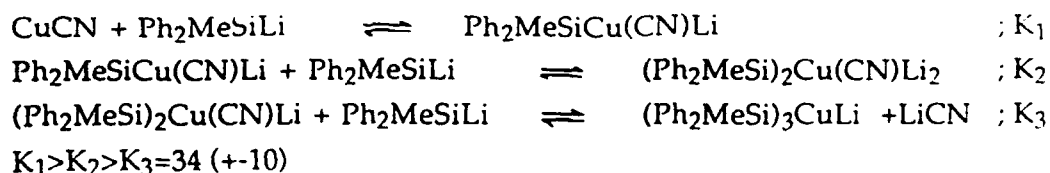
New Initiators for the Ring-Opening Polymerization

We have previously reported on the anionic polymerization of the mixture of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilanes with silyl potassium and butyl lithium as initiators in relatively non-polar media (benzene with less than 5% THF), sometimes in the presence of crown ethers and cryptands (cryptand [2.1.1] which is selective for lithium). Polysilylenes with molecular weights up to $M_n=50,000$ were prepared at ambient temperatures. Silyl anions are very reactive species and they may not only induce ring-opening of the strained cycle (propagation) but also lead to either dearylation or demethylation of the ring (transfer/termination). Silyl anions may also loose an electron and form silyl radicals which will very rapidly react with a solvent. Silyl anions, especially accompanied by cryptated Li cations, may react with various impurities:



(3)

In order to increase selectivity of silyl anions we attempted their modifications by adding copper cyanates which form various types of complexes. Up to three silyl moieties can be coordinated with Cu atom. The catalytic efficiency is the highest for the ratio Si/Cu=2. Equilibrium constants for the complexation decreases with the number of Si moieties:



(4)

Silyl cuprates are active in THF solution and complete polymerization with less than 1 mol% of the initiator. Monomers purified in the same way require at least 2 mol% of *n*BuLi as the initiator. This may indicate higher selectivity and lower sensitivity for impurities of copper based initiators. Moreover, no depolymerization to strainless cycles was observed in THF with Cu containing initiators. In contrast, BuLi in THF gives within 5 minutes complete depolymerization of linear chains.

One of the most interesting aspects of Cu/2Si initiator is the control of tacticities. As shown in Fig. 3, three relatively sharp signals of poly(methylphenylsilylene) are observed in the contrary to a very broad signal found with BuLi initiator. In both cases the same enriched (>90%) "all-trans" isomer was used. It seems that Cu/2Si species react with a monomer with the retention of configuration on the attacked Si atom. Unmodified silyl lithium has lower stereoselectivity and allows also inversion.

Thus, the application of copper modified catalysts leads to more selective and slower polymerization, reduced amount of macrocyclics and to considerable increase of the stereoselectivity of the ring opening process.

It has been previously reported that disilane can be metathesized in the presence of palladium based catalysts and rings containing disilane bond (e.g. 1,1,2,2-tetramethyl-1,2-disilacyclopentane) can be dimerized¹². We have used various Pd and Pt based homogeneous catalysts for polymerization of cyclotetrasilanes. We found that usually the reaction in the presence of 2 mol% of Pd(PPh₃)₄ leads to the formation of dimers in high (>90%) yield. Size

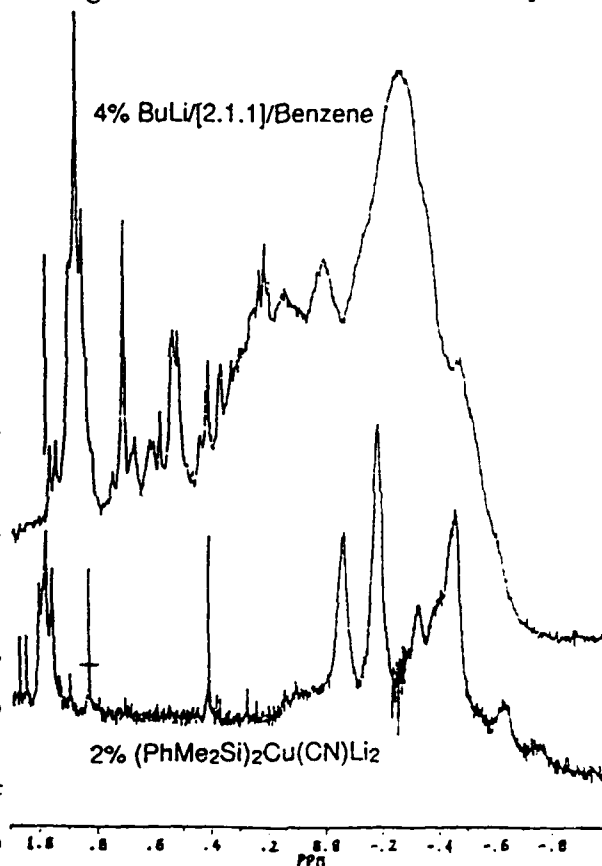


Fig.3. 300 MHz ¹H NMR spectra of polymers obtained by polymerization of enriched (>90%) all-trans 1,2,3,4-tetramethyl-1,2,3,4-tetra phenylcyclotetrasilane initiated by 4 mol% of BuLi (with cryptand [2.1.1]) in benzene and 2 mol% of (PhMe₂Si)₂Cu(CN)Li₂ in THF at RT.

exclusion chromatography shows one peak with a retention time corresponding to species with $M=950$. Mass spectroscopy (SIMS) confirms a dimer structure (cf. observed and simulated MS spectra for the dimer). ^1H NMR spectra of dimers prepared from the mixture of various stereoisomers of cyclotetrasilanes are very complicated. On the other hand a relatively simple spectrum is obtained for a dimer prepared from the enriched "all-trans" isomer:

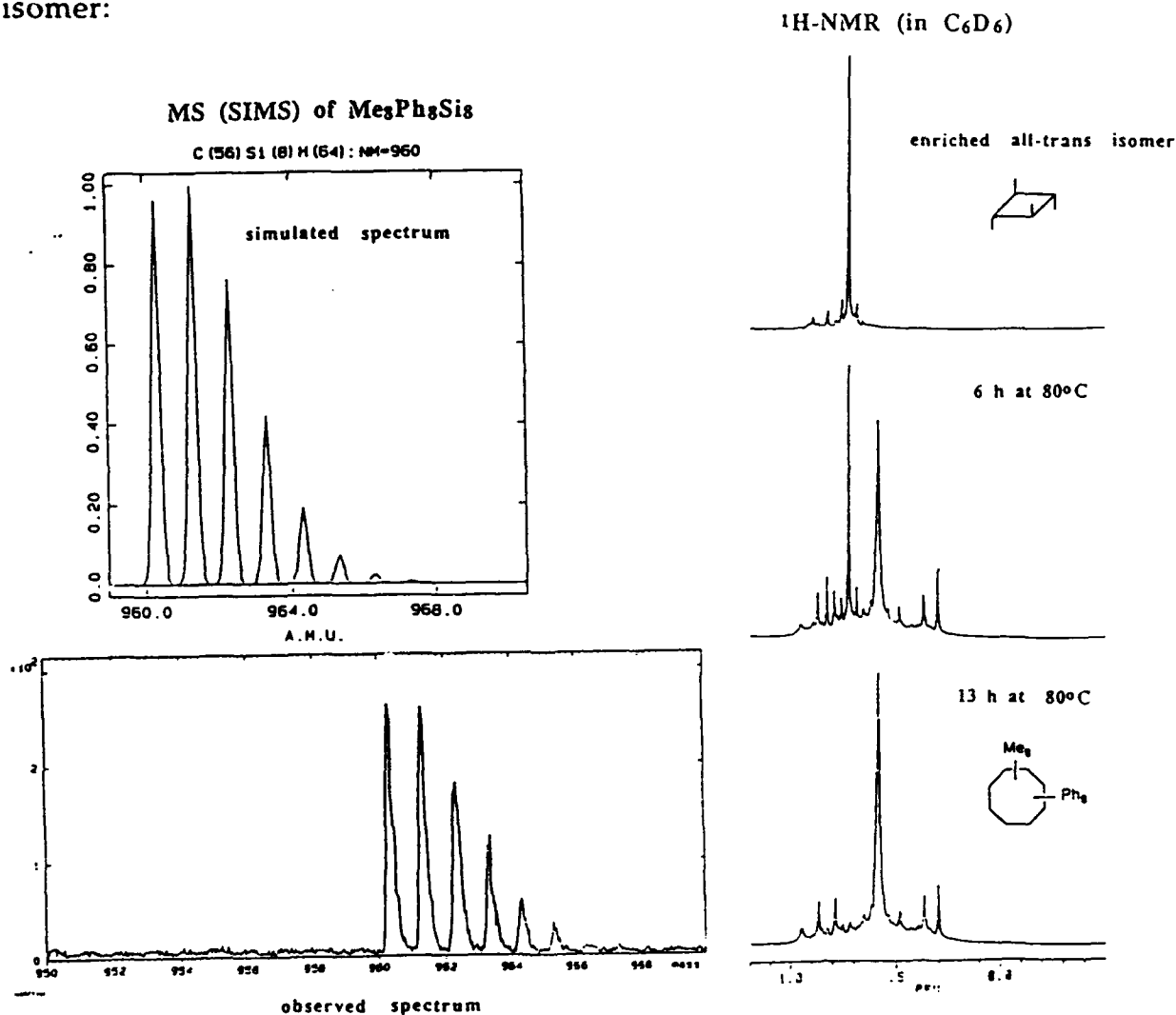


Fig.4. Mass spectra (SIMS) of the cyclooctasilane (simulated and observed spectra)

Fig. 5. ^1H NMR spectra of enriched "all-trans" cyclotetrasilane during conversion to a dimer in the presence of $\text{Pd}(\text{PPh}_3)_4$

This may indicate high stereoselectivity for this reaction (probably all-trans eight-membered ring is formed). Dimers are the main products in the reaction catalyzed by transition metals containing bulky ligands (PPh_3). Smaller ligands provide also linear chains. This process is strongly accelerated in the presence of moisture and oxygen. It seems that linear Si-Si catenation is interrupted in these polymers by Si-O-Si linkages which can be formed by hydrolytic polymerization or oxygen insertion. The obtained polymers absorb at shorter wavelengths (<300 nm) in contrast to 340 nm observed for poly(methylphenylsilylene). This again confirms incorporation of oxygen to a

backbone which reduces delocalization of the electrons¹³ in polysilylene backbone.

We focus our current research on the catalysts which will provide linear polysilylenes with high chemoselectivity, regioselectivity, and stereoselectivity.

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